

Amendments to the Specification

On page 1, line 28 to page 2, line 4, please replace the paragraph set forth therein with the following:

Conducting polymers, such as polythiophenes (PTs), represent a class of polymers that are lightweight, highly processable and exhibit relatively high environmental stability, thermal stability, and electrical conductivity. These materials can be synthetically tailored to achieve desired properties such as melting point, electrical conductivity, optical and microwave absorbance and reflectance, and ~~electroluminescence~~ electroluminescence. Compared to inorganic metals and semiconductors, electrically conductive polymers have been found to be promising candidates for numerous applications, ranging from electronic and optical devices, such as field-effect transistors, sensors, light-emitting diodes (LEDs), rechargeable batteries, smart cards, and non-linear optical materials, to medical applications, such as artificial muscles.

On page 2, lines 13-24, please replace the paragraph set forth therein with the following:

Techniques that incorporate blends and/or composites of conducting polymers and conventional polymers include chemical and electrochemical *in situ* polymerizations. These methods include mechanically mixing two or more conducting and conventional polymers to form a polymer blend. Blending methods are relatively simple and cost effective when compared to methods that produce block copolymers, and can be found in various publications, such as, for example, H. L. Wang, L. Toppare, J. E. Fernandez, *Macromolecules*, 23, 1053 (1990); K. Koga, S. Yamasaki, K. Narimatsu, M. Takayanagi, *Polym. J.* 1989, 21(9), 733 (1989); *Synthetic Metals*, 21, 41 (1989); *Synthetic Metals*, 28, c435 (1989); *Synthetic Metals*, 37, 145 (1990); *Synthetic Metals*, 37, 195 (1990); *Macromolecules*, 25, 3284 (1992); *Synthetic Metals*, 22, 53 (1987); *Macromolecules*, 22, 1964 (1989); *Polymer*, 39, 1992

(1989)[[:]] and U.S. Patent Nos. 5,427,855 and 5,391,622.

On page 3, lines 11-20, please replace the paragraph set forth therein with the following:

The second approach to improve the processability and mechanical properties of electrically conductive polymers is through the synthesis of block copolymers. Block copolymers are typically formed from the reaction of conducting polymers and conventional polymers (i.e. structural polymers such as polystyrenes, polyacrylates, polyurethanes, and the like), the product of which ~~exhibit~~ exhibits a combination of the properties of their segment polymers. Accordingly, segment polymers can be chosen to form copolymer products having attractive mechanical properties. Furthermore, the covalent linkage between the polymer segments allows phase separation to be limited at the molecular level, thereby providing a more homogeneous product relative to polymer blends.

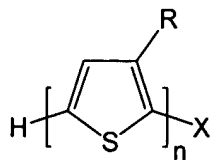
On page 4, lines 9-15, please replace the paragraph set forth therein with the following:

The discovery of additional applications and new technologies for conductive block copolymers is subject, in large part, to molecular ~~designers~~ designer's ability to control the structure, properties, and function of their chemical synthesis. Those in the art have come to recognize that structure plays an important, if not critical role, in determining the physical properties of conducting polymers. PTs represent a class of conducting polymers that are thought to have the potential for furthering the advancement of new and improved applications for conductive block copolymers.

On page 7, line 16 to page 8, line 4, please replace the paragraph set forth therein with the following:

The present invention also provides a method of forming a polymer

that includes combining a soluble thiophene monomer with an amide base and a divalent metal halide, and adding an effective amount of a first Ni(II) catalyst to initiate a polymerization reaction to form at least 90% by weight of an intermediate polymer having the structure:



wherein R is a substituent selected from the group consisting of alkyl, polyether, and aryl, X is a halogen, and n is greater than 1. Added to the intermediate polymer is a derivative compound represented by the formula PFG-A-MX' and a second Ni(II) catalyst to form a protected thiophene polymer, wherein PFG is a hydroxyl or amine functional group, A is selected from the group consisting of alkyl and aromatic, M is **[[a]]** selected from the group consisting of Zn or Mg, and X' is a halogen. The thiophene polymer is deprotected in an acid environment to form the deprotected polymer having one functional end group.

On page 8, lines 5-15, please replace the paragraph set forth therein with the following:

In another embodiment, the present invention provides a method of forming a polymer that includes combining a soluble thiophene monomer with an amide base and zinc chloride at a temperature ranging from -78°C to -60°C and adding an effective amount of a first Ni(II) catalyst to initiate a polymerization reaction and form an intermediate polymer. A derivative compound represented by the formula PFG-A-MX' and a second Ni(II) catalyst is added to the intermediate polymer to form a protected thiophene polymer, wherein PFG is a hydroxyl or amine functional group, A is selected from the group consisting of alkyl and aromatic, M is **[[a]]** selected from the group consisting of Zn or Mg, and X' is a halogen. The protected thiophene polymer is deprotected in an acid environment to form the deprotected polymer having one functional end group.

On page 8, lines 21-27, please replace the paragraph set forth

therein with the following:

The present invention also provides a deprotected polymer having one functional end group having the structure:



wherein R is selected from the group consisting of alkyl, polyether, and aryl; n is greater than 1; A is selected from the group consisting of alkyl and aromatic[[.]]; and FG is a functional group selected from the group consisting of primary alkyl amine and primary alcohol.

On page 9, line 21 to page 10, line 9, please replace the paragraph set forth therein with the following:

The present invention also provides a method of forming a diblock copolymer that includes combining a soluble thiophene monomer with an amide base and zinc chloride at a temperature ranging from -78°C to -60°C and adding an effective amount of a first Ni(II) catalyst to initiate a polymerization reaction and form an intermediate polymer. A derivative compound represented by the formula PFG-A-MX' and a second Ni(II) catalyst is added to the intermediate polymer to form a protected thiophene polymer, wherein PFG is a hydroxyl or amine functional group, A is selected from the group consisting of alkyl and aromatic, M is [[a]] selected from the group consisting of Zn or Mg, and X is a halogen. The protected thiophene polymer is deprotected in an acid environment to form a deprotected polymer having one functional end group. An ATRP initiator and a base are added to the deprotected polymer to form an ATRP macroinitiator. CuBr, at least one ATRP ligand, and at least one radically polymerizable monomer are added to the ATRP macroinitiator to form the diblock copolymer.

On page 10, lines 10-19, please replace the paragraph set forth therein with the

following:

Another method of forming a diblock copolymer is presented herein, and includes providing a deprotected polymer having one functional end group having the structure:



wherein R is selected from the group consisting of alkyl, polyether, and aryl; n is greater than 1; A is selected from the group consisting of alkyl and aromatic; and FG is a functional group selected from the group consisting of primary alkyl amine and primary alcohol. An ATRP initiator and a base are added to the deprotected polymer to form an ATRP macroinitiator. CuBr, at least one ATRP ligand, and at least one radically polymerizable monomer are added to the ATRP macroinitiator to form the diblock copolymer.

On page 19, lines 21-23, please replace the paragraph set forth therein with the following:

Polymer 5 may be reacted with at least one equivalent of an organomagnesium (Grignard) reagent, in refluxing solvent, for a sufficient period of time, typically at least one hour, and then quenched to produce polymer 6.

On page 12, lines 10-20, please replace the paragraph set forth therein with the following:

The incorporation of the end group functionalized HT-PATs into block copolymers is shown in Schemes 3, 4, and 5. In Schemes 3 and 4, atom-transfer-radical-polymerization (ATRP) is used to incorporate the HT-PATs with some conventional polymers such as polystyrene and polyacrylates. ATRP is a well-developed "living" radical polymerization that generates well-defined polymers, representative methods of which are described in Wang, J.-S. and Matyjaszewski, K., *J. Am. Chem. Soc.*, 117, 5614-5615 (1997); Patten, T. E.,

Xia, J, Abernathy, T., and Matyjaszewski, K., *Science*, 272, 866-868 (1996); Matyjaszewski, K., ~~Patten~~ Patten, T. E., and Xia, J., *J. Am. Chem. Soc.*, 119, 674-680 (1997); and Matyjaszewski, K., Gobelt, B., Paik, H.-J., and Horwitz, C. P., *Macromolecules*, 34, 430-440 (2001), each of which is incorporated by reference herein in its entirety.

On page 12, lines 10-20, please replace the paragraph set forth therein with the following:

Thin films of PHT-PS and PHT-PA (i.e. products of Scheme 3), PS-PHT-PS and PA-PHT-PA (i.e. products of Scheme 4), and polyurethane elastomers (i.e. the product ~~the~~ of Scheme 5), were generated by the slow evaporation of toluene solutions to give magenta to purple films with excellent mechanical properties. These films were oxidized by exposure to I₂ vapor to give multifunctional polymers with high electrical conductivities (Table 1) as determined by four-point probe conductivity measurements.

On page 27, lines 2-4, please replace Table 1 set forth therein with the following:

PS-PHT Diblock Copolymers				
wt% of HT-PHT ^a	100%	37%	22%	14%
Average M _n ^b	16,800	30,20	41,400	53,400
		0		
M _w /M _n ^b	1.28	1.31	1.32	1.45
Conductivity (S/cm)	110	4.7	0.08	0.14
PS-PHT-PS Triblock Copolymers				
wt% of HT-PHT ^a	100%	52%	26%	7.7%
Average M _n ^b	17,900	25,50	38,100	93,600
		0	<u>38,100</u>	
M _w /M _n ^b	1.23	1.21	1.25	1.51
Conductivity (S/cm)	96	5.3	0.43	0.05
PA-PHT-PA Triblock Copolymers				
wt% of HT-PHT ^a	100%	45%	18%	10%
Average M _n ^b	17,900	29,70	50,400	72,300
		0		

M_w/M_n^b	1.23	1.29	1.41	1.66
Conductivity (S/cm)	96	3.3	1.6	0.076
Polyurethane				
wt% of HT-PHT	10%	6.40%	0.60%	
Conductivity (S/cm)	0.13	0.48	4.6×10^{-5}	

On page 27, line 9 to page 28, line 7, please replace the paragraph set forth therein with the following:

It has been found that certain embodiments of the present invention exhibit high electrical conductivities. While many copolymers containing conjugated polymers and other polymers and blends have been prepared, it is believed that the excellent conductivity values exhibited by the copolymers of the present invention, as illustrated in Table 1, have not been reported. While 100% HT-PHT has a conductivity of 110 S/cm, PHT-PS (Scheme 3) has a conductivity of about 5 S/cm for a block copolymer containing 37% HT-PHT. The conductivity drops down to 0.1 S/cm for samples containing approximately 22% of HT-PHT or less. The conductivity of the block copolymers largely depends on the ratio of the conducting blocks and the non-conducting blocks, which relates to the structural assembly. The PS-PHT-PS triblock copolymers (Scheme 4) have conductivities as high **[[a]]** as 5 S/cm for a sample with 52% PHT. The conducting polymer polyurethane copolymers (Scheme 5) exhibit conductivities of as high as 10^{-1} S/cm, which is much higher than other polyurethane conjugative copolymers or blends reported in literature (10^{-4} S/cm). Conductivities for blends of conjugative polymers with polyvinylchloride and other conventional polymers have also been found to exhibit low conductivities of about 10^{-4} S/cm range.

On page 29, lines 17-28, please replace the paragraph set forth therein with the following:

Due to the nanophase separation of block copolymers, the HT-PAT

blocks copolymers of the present invention tend to self-assemble into nanoscale domains. In these worm-like domains HT-PAT chains are fully extended and tightly packed together. These highly ordered π - π stacking structures make the domains highly conductive nanowires. TEM, AFM and X-ray diffraction have confirmed the ~~present~~ presence of the nanowire network in these copolymers. Because of the presence of a nanowire network, the block copolymers of the present invention have much higher electrical conductivity than any other conducting blends/composites or copolymers previously reported. In addition, the block copolymers synthesized by this method can form highly smooth coatings when cast from solution. Films of these block copolymers have much better adhesion to substrates such as glass, steel and plastics than HT-PATs. Upon doping their morphology remains uniform, and the films do not crack.

On page 29, line 29 to page 30, line 12, please replace the paragraph set forth therein with the following:

It has been found that novel nanowires morphologies in block copolymers of regioregular poly(alkylthiophenes) of the present invention provide the possibility of guiding the intrinsic self-assembly of sufficiently regular conjugated polymer chains by coupling them chemically to incompatible segments. In the simplest case, the obtained structure is the result of interplay between different driving forces of self-assembly (π -stacking vs. phase separation). Accordingly, due to strong π -interactions, the free energy landscape of rigid conjugated molecules has few deep local minima, which cannot be easily explored under normal conditions. Thus the molecules are easily trapped in the states with high extent of local stacking but at the same time with high concentration of defects adversely affecting the bulk properties. Copolymerization with incompatible flexible segments may result in competing driving forces of self-assembly resulting in relatively easier to explore free energy landscapes. Identifying the overall features of those energy landscapes may **[[give]]**provide the ability to exercise control of the resulting nanostructures, and

effectively provide ways to apply conjugated polymers as building blocks for future nanoscale- and molecular level electronic devices.

On page 30, lines 13-21, please replace the paragraph set forth therein with the following:

The block copolymers in their undoped state may be used as field-effect transistor materials due to the ~~present~~ presence of highly ordered nanowire network structures. Friend et ~~al.~~ al. have reported the using of HT-PATs as field-effect transistor materials (Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marks, R. N., Mackay, K., Friend, R. H., Burns, P. L., Holmes, A. R., *Nature* (London), 347, 539 (1990); Bao, Z., Dodabalapur, A., Lovinger, A. J., *Appl. Phys. Lett.*, 69, 4108 (1996)). The field-effect mobilities of the block copolymers described here can be as high as $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Additionally, the block copolymers in their undoped state can be used as dielectric materials.

On page 32, lines 9-21, please replace the paragraph set forth therein with the following:

The HT-PHT with well-defined H/Br end group structure was then used to perform the end group modification. To a 100ml flask were added 20ml anhydrous THF and 0.708g of 2-(2-thienylethoxy)tetrahydro-2H-pyran (0.0025mol). The flask was cooled to -40°C and 1ml of butyllithium solution (2.5M) was added. The solution was kept at -40°C for 30 minutes, followed by the addition of 0.8g of anhydrous ZnCl_2 . The solution was then slowly warmed up to room temperature. This organozinc solution was transferred to a THF (30 ml) solution with 0.29 of HT-PHT with HBr end group. After the addition of 0.08g of Ni(dppp)Cl_2 , the solution was kept stirring at 60°C for 5 hours. The polymer was then precipitated out in methanol and purified by reprecipitation. This polymer was deprotected with HCl/THF mixture at 40°C for ~~three hour~~ 3 hours and then precipitated in methanol. After filtration and drying, HT-PHT with -OH

functional group was obtained with a yield of 95%. Figure 1 and Figure 2 show respectively the NMR and MALDI of this hydroxy functionalized head-to-tail poly(3-hexylthiophene).

On page 32, line 26 to page 33, line 11, please replace the paragraph set forth therein with the following:

The synthesis was carried out as illustrated in Scheme 2. HT-PHT (0.3g, 0.04mmol) was dissolved in anhydrous THF (80ml). 2M t-butylMgCl in THF (5ml) was then added. The mixture was warmed to 70°C ~~[[at]]~~ and stirred at that temperature for 2 hours. After cooling to room temperature, 2M HCl aqueous solution (5ml) was added to neutralize the solution. After precipitated in methanol and purified by Soxhlet extraction, the polymer was dissolved in anhydrous toluene (80ml) under nitrogen. N-methylformanilide (2ml, 0.016mol) and POCl₃(1.3ml, 0.014mol) were then added. The reaction was carried out at 75°C for 24 hours. The solution was cooled to room temperature, followed by adding saturated aqueous solution of sodium acetate. The solution was stirred for another 2 hours. The polymer was precipitated in methanol and purified by ~~Sexlet~~ Soxhlet extraction with methanol. After drying in vacuum, the polymer was dissolved in anhydrous THF (80ml) under nitrogen. LiAlH₄ solution in THF (1M, 1.0ml) was then added. The mixture was stirred at room temperature for 40 minutes. HCl (1 M, 1 ml) was then added to quench the excess LiAlH₄. The polymer was precipitated in methanol and purified by Soxhlet extraction with methanol. After drying in vacuum, HT-PHT diol was obtained. Yield was recorded to be 93%. Figure 3 is the MALDI MS of the product.

On page 33, lines 16-31, please replace the paragraph set forth therein with the following:

The preparation was performed as shown in Scheme 3. -OH functionalized HT-PHT (0.14g, 0.018mmol) was dissolved in anhydrous THF (40ml) under nitrogen. To the solution triethylamine (3.0ml, 0.022mol) and 2-

bromopropionyl bromide (2.5ml, 0.02mol) were added. The reaction was carried out at room temperature for about 12 hours. The polymer was precipitated in methanol and purified through dissolving in THF and precipitation again in methanol. After drying in vacuum, this macroinitiator (0.1g, about 0.012mmol) was dissolved in the mixture of styrene (7ml) and toluene (7ml). The styrene has been freshly distilled under vacuum to eliminate the inhibitor. The toluene was also freshly distilled. To this polymer solution CuBr (0.036g, 0.25mmol) and N,N,N',N'-pentamethyldiethylenetriamine (PMDTA) (0.043g, 0.25mmol) were added. The solution was then purged with nitrogen for 20 minutes and placed into an oil bath of 90°C. 5ml of the solution was removed by syringe to precipitate the polymer in methanol after 0.5 hours, 1.5 hours, 3.0 hours, and 4.5 hours respectively. The diblock copolymers were dissolved in THF and ~~passed~~ passed through the Al₂O₃ column to eliminate the catalyst. Pure copolymers were obtained after precipitation in methanol again. All four copolymers were a purple powder.

On page 34, lines 16-26, please replace the paragraph set forth therein with the following:

The electrical conductivities of these diblock copolymers were measured using the routine four-point probe method. The block copolymer solutions in toluene (5mg/1 ml) were cast on glass slides. These solid films were then ~~exposed~~ exposed to an iodine atmosphere for 10 hours. Thereafter, the four-point probe method was used to measure the resistance of the films. At least 6 times of repeating measurement were carried for a selected area. Each of the glass slides with polymer films was then dipped into liquid nitrogen and broken into two pieces at the selected area. Because the temperature was much lower than the T_g of the copolymers, the breaking cross sections were clean and flat. Scanning Electron Microscopy (SEM) was then employed to measure the width of the cross sections of the selected areas. The conductivity (σ) was obtained with the following:

On page 35, lines 10-14, please replace the paragraph set forth therein with the following:

The synthesis is the same as that described in Example 4 except that methyl acrylate monomer was used in the ATRP step. NMR and size exclusion chromatography also were used to characterize these diblock copolymers. The characterization results are listed in Table 3.

On page 35, lines 21-24, please replace the paragraph set forth therein with the following:

Both AFM and TEM have confirmed the ~~present~~ presence of "nano-wire" networks in the solid films of the diblock copolymers casted from their solution in toluene or xylene. Figure 5 and Figure 6 respectively show the AFM and TEM of a HT-PHT-block-PMA sample.

On page 35, lines 25-26, please replace the paragraph set forth therein with the following:

The conductivity measurement of these diblock copolymers ~~were~~ was performed in the same way as described in Example 3. The results are also listed in Table 3.